

Crystals **2012**, *2*, 974–983; doi:10.3390/cryst2030974

OPEN ACCESS

crystals

ISSN 2073-4352

www.mdpi.com/journal/crystals

Article

1,5-Diaminopentane As A Structure-Directing Agent for Zincophosphate Networks: $\text{Zn}_3(\text{PO}_4)_2(\text{C}_5\text{H}_{14}\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ and $\text{C}_5\text{H}_{16}\text{N}_2 \cdot \text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$

William T.A. Harrison * and William R. Currie

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, UK; E-Mail: curriedbill@gmail.com

* Author to whom correspondence should be addressed; E-Mail: w.harrison@abdn.ac.uk; Tel.: +44-1224-272897; Fax: +44-1224-272921.

Received: 5 June 2012; in revised form: 28 June 2012 / Accepted: 3 July 2012 /

Published: 16 July 2012

Abstract: The crystal structures of two zincophosphate networks prepared in the presence of 1,5-diaminopentane (dap) are described. In $\text{Zn}_3(\text{PO}_4)_2(\text{C}_5\text{H}_{14}\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ (**1**) the dap forms Zn–N coordinate bonds to generate an unusual three-dimensional “hybrid” framework constructed from ZnO_3N , ZnO_2N_2 and PO_4 tetrahedra with three different types of elongated channels occupied by water molecules. In $\text{C}_5\text{H}_{16}\text{N}_2 \cdot \text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$; (**2**) the doubly-protonated H_2dap acts in a more typical way to template double layers of vertex-sharing ZnO_4 , PO_4 and HPO_4 tetrahedra incorporating 10-rings and interacts with the inorganic component *via* N–H O hydrogen bonds. Crystal data: **1** ($\text{C}_{10}\text{H}_{34}\text{N}_4\text{O}_{11}\text{P}_2\text{Zn}_3$), $M_r = 644.46$, monoclinic, $C2$ (No. 4), $Z = 4$, $a = 25.302$ (7) Å, $b = 4.9327$ (13) Å, $c = 19.808$ (6) Å, $\beta = 107.377$ (8)°, $V = 2359.4$ (12) Å³, $R(F) = 0.054$, $wR(F^2) = 0.139$. **2** ($\text{C}_5\text{H}_{19}\text{N}_2\text{O}_{13}\text{P}_3\text{Zn}_3$), $M_r = 604.24$, monoclinic, $P2_1/c$ (No. 14), $Z = 4$, $a = 11.3275$ (15) Å, $b = 8.3235$ (11) Å, $c = 18.588$ (2) Å, $\beta = 96.979$ (3)°, $V = 1739.6$ (4) Å³, $R(F) = 0.056$, $wR(F^2) = 0.119$.

Keywords: zincophosphate; framework; template; hydrogen bonds

1. Introduction

Linear-chain alkyl diamines of formula $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ are versatile and effective templates for a wide variety of porous inorganic networks incorporating many different metal ions [1–4]. As might be

expected, the chain length n of the methylene groups of the diamine plays an important role in defining the resulting crystal structure: this is demonstrated with diamine-templated zinc phosphates (ZnPOs) and varied structures with $n = 2$ (*i.e.*, ethylenediamine) [5], $n = 3$ [6], $n = 4$ [7] and $n = 6$ [8] have been described.

As an extension of these studies we now describe the structures of two zincophosphate networks incorporating the $n = 5$ member of this series, 1,5-diaminopentane [$\text{H}_2\text{N}(\text{CH}_2)_5\text{NH}_2$; $\text{C}_5\text{H}_{14}\text{N}_2$; dap], as the structure-directing agent. In $\text{Zn}_3(\text{PO}_4)_2(\text{C}_5\text{H}_{14}\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ (**1**) the neutral dap molecule bonds directly to the zinc ions as a bridging ligand to generate an unusual structure containing elongated “hybrid” channels containing water molecules, whereas in $\text{C}_5\text{H}_{16}\text{N}_2 \cdot \text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$; (**2**) doubly-protonated H_2dap dications help to template a layered ZnPO network *via* N-H \cdot O hydrogen bonds. So far as we are aware, there are no other known dap-ZnPO structures, although H_2dap dications have been shown to template zinc phosphite (containing HPO_3^{2-} groups) [9] and zinc diphosphonate [10] materials.

2. Results and Discussion

2.1. Crystal Structure of $\text{Zn}_3(\text{PO}_4)_2(\text{C}_5\text{H}_{14}\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ (**1**)

The asymmetric unit of compound **1** contains four Zn atoms, two P atoms, 11 O atoms (three of which belong to water molecules) and two $\text{C}_5\text{H}_{14}\text{N}_2$ (dap) molecules (Figure 1).

Figure 1. The asymmetric unit of **1** (50% displacement ellipsoids) expanded to show the Zn coordination spheres. Atoms with a * suffix to their labels are symmetry generated (see Table 1).

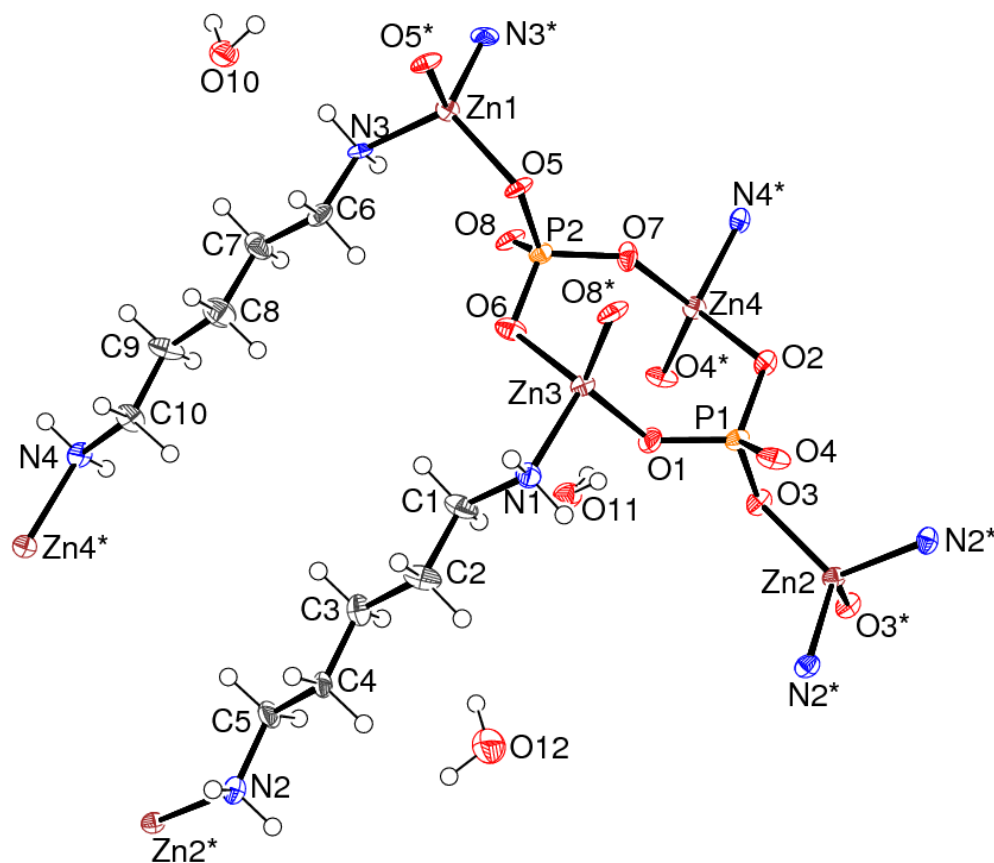


Table 1. Selected bond distances (Å) and angles (°) in **1**.

Bond	Distance	Bond	Distance
Zn1-O5	1.964 (9)	Zn1-N3	2.037 (13)
Zn2-O3	1.914 (9)	Zn2-N2#1	2.027 (11)
Zn3-O8#2	1.914 (10)	Zn3-O1	1.933 (7)
Zn3-O6	1.943 (11)	Zn3-N1	2.032 (10)
Zn4-O2	1.939 (10)	Zn4-O7	1.942 (7)
Zn4-O4#3	1.949 (9)	Zn4-N4#4	2.055 (10)
P1-O4	1.516 (12)	P1-O2	1.542 (8)
P1-O3	1.543 (8)	P1-O1	1.550 (8)
P2-O5	1.526 (8)	P2-O8	1.537 (13)
P2-O7	1.549 (8)	P2-O6	1.551 (8)
Bond	Angle	Bond	Angle
P1-O1-Zn3	130.4 (5)	P1-O2-Zn4	115.3 (5)
P1-O3-Zn2	125.2 (7)	P1-O4-Zn4#2	128.2 (6)
P2-O5-Zn1	121.7 (7)	P2-O6-Zn3	114.3 (5)
P2-O7-Zn4	132.6 (6)	P2-O8-Zn3#3	128.5 (6)

Symmetry codes: (#1) $\frac{1}{2}-x, y-\frac{1}{2}, 1-z$; (#2) $x, y-1, z$; (#3) $x, y+1, z$; (#4) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

The zinc ions in **1** adopt two coordination modes: Zn1 and Zn2 (which both lie on crystallographic twofold axes) are coordinated by two O and two N atoms and Zn3 and Zn4 are bonded to three O and one N atom in tetrahedral geometries (Table 1). The global mean Zn-O and Zn-N separations are 1.937 Å and 2.038 Å, respectively, which are very similar to the equivalent geometrical data for related compounds [11]. The XO_4 tetrahedral angular variances, defined as $\frac{1}{5} \sum_{j=1}^6 (\vartheta_j - 109.47)^2$ where ϑ is the O-X-O bond angle (°) [12], indicate that all the Zn-centred tetrahedra in **1** are significantly distorted: values of $98.4^{\circ 2}$, $79.8^{\circ 2}$, $81.2^{\circ 2}$ and $85.9^{\circ 2}$ arise for Zn1, Zn2, Zn3 and Zn4, respectively. All the O atoms also link to an adjacent P atom (mean Zn-O-P = 124.5°) and the N atoms are all parts of neutral dap molecules. Both PO_4 groups in **1** are close to regular tetrahedra (mean P1-O = 1.538 Å, angular variance = $2.7^{\circ 2}$; mean P2-O = 1.541 Å, angular variance = $1.4^{\circ 2}$) and all the O atoms link to an adjacent Zn atom, thus there are no terminal or “dangling” P=O or P-OH bonds [13] in **1**. The geometrical parameters for the two unique dap molecules are unexceptional [14], and both molecules are in essentially extended conformations (mean absolute values of the N-C-C-C and C-C-C-C torsion angles = 177.6° and 174.7° , respectively).

The polyhedral connectivity of the Zn- and P-centred moieties leads to (100) sheets of vertex-sharing tetrahedra (Figure 2), in which there is perfect alternation of the Zn and P nodes (*i.e.*, no Zn-O-Zn or P-O-P links). These sheets can be decomposed into four-ring ladders [15] propagating in [010] built up from the Zn3- and Zn4-centred species and the phosphate groups, with Zn1 and Zn2 (*i.e.*, the ZnN_2O_2 species) providing inter-chain links, as parts of polyhedral 8-rings. For any [010] stack of 8-rings, all the Zn1 (or Zn2) tetrahedra point in the same direction.

The dap molecules form bridges (*via* both their N atoms) to the adjacent (100) polyhedral sheets to generate a distinctive porous network (Figure 3), in which elongated [010] channels are bounded by the methylene groups of the dap molecules on their “long” sides and by the ZnPO framework on their “short” sides. Measured atom-to-atom, their dimensions are about $4.5 \text{ Å} \times 11.3 \text{ Å}$. It is remarkable that

there are three distinct types of channel in this structure: one contains four water molecules per *b* unit-cell repeat distance (type-A), one contains two water molecules (type-B) and the third (type-C) is empty. It is apparent from Figure 3 that the type-A channels “bulge out” to accommodate the water molecules and the type-C channels are consequently compressed inwards and are empty.

Figure 2. Part of a (100) tetrahedral sheet in **1**. Color key: Zn tetrahedra yellow, P tetrahedra green, O atoms red, N atoms blue.

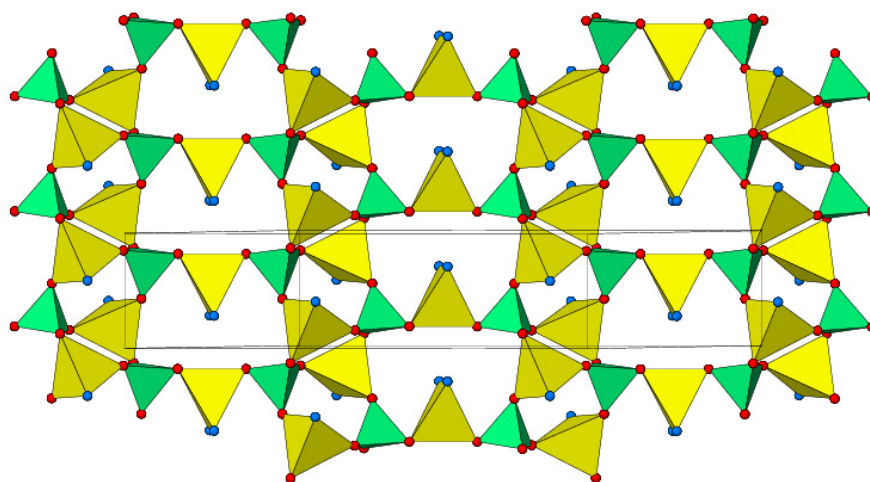
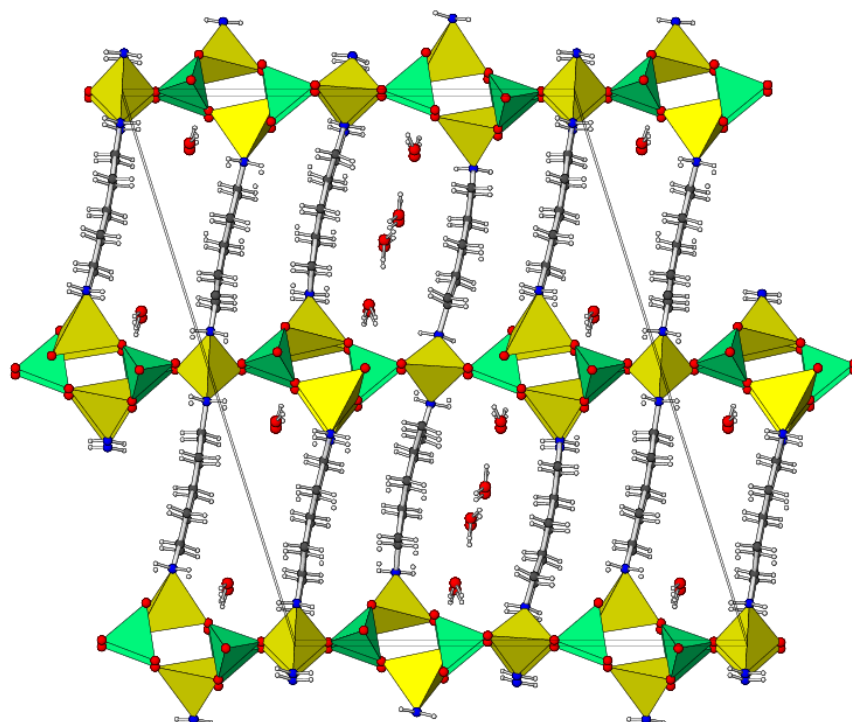


Figure 3. View approximately down [010] of the unit-cell packing in **1**, showing the three types of elongated channels with different water-molecule occupancies (see text). Color key as for Figure 2; in addition, C dark grey, H white.



Within the type-A channel, the water molecules interact *via* O-H...O hydrogen bonds (Table 2), such that a C(2) chain of O12-H6W...O12 bonds propagates up the central region of the channel. The other H atom attached to O12 forms a link to O11, which in turn forms two hydrogen bonds to

framework O atoms. The -NH_2 groups of the dap molecules form $\text{N-H}\cdots\text{O}$ hydrogen bonds to framework O atoms as well as the water molecules to reinforce this rather intricate network, which occurs in a largely hydrophobic environment.

Table 2. Hydrogen bond geometries (\AA and $^\circ$) in **1**.

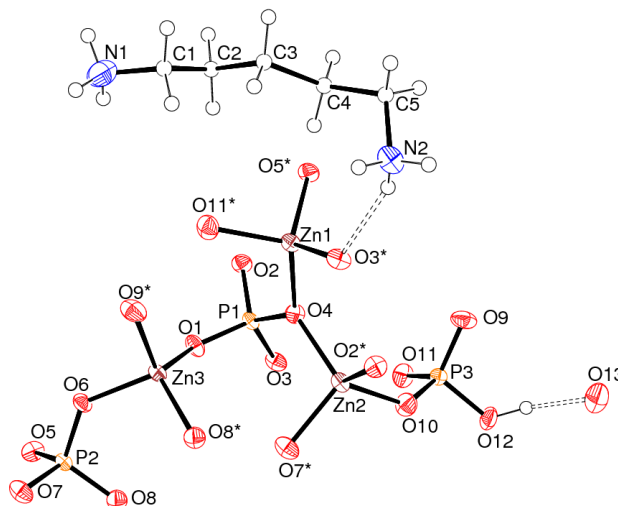
Bond	D-H	H \cdots A	D \cdots A	D-H \cdots A
N1-H1A \cdots O11#2	0.92	2.24	3.138 (14)	164
N1-H1B \cdots O6#2	0.92	2.46	2.981 (16)	116
N2-H2C \cdots O3#5	0.92	2.30	3.131 (16)	149
N2-H2D \cdots O11#1	0.92	2.47	3.245 (11)	142
N2-H2D \cdots O3#1	0.92	2.58	3.196 (16)	125
N3-H3C \cdots O10	0.92	2.44	3.158 (11)	136
N3-H3C \cdots O5#6	0.92	2.49	3.152 (16)	129
N3-H3D \cdots O5#3	0.92	2.28	3.081 (17)	145
N4-H4D \cdots O10#7	0.92	2.08	2.971 (14)	164
O10-H1W \cdots O7#6	0.90	1.89	2.723 (15)	152
O10-H2W \cdots O8#8	0.90	2.14	2.928 (11)	145
O11-H3W \cdots O4#3	0.91	2.30	2.973 (11)	131
O11-H4W \cdots O1	0.90	1.84	2.734 (15)	171
O12-H5W \cdots O11#1	0.90	2.07	2.941 (10)	164
O12-H6W \cdots O12#9	0.90	1.97	2.838 (7)	160

Symmetry codes as Table 1; additionally: (#5) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (#6) $-x, y+1, -z$; (#7) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (#8) $-x, y, -z$; (#9) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$.

2.2. Crystal Structure of $\text{C}_5\text{H}_{16}\text{N}_2\cdot\text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4)\cdot\text{H}_2\text{O}$ (**2**)

The asymmetric unit of **2** contains three Zn atoms, two PO_4 groups, one HPO_4 group, a water molecule and a doubly-protonated H_2dap dication (Figure 4).

Figure 4. The asymmetric unit of **2** (50% displacement ellipsoids; indicative spheres for the C atoms), expanded to show the complete coordination spheres of the zinc atoms. Atoms with a * suffix are symmetry generated (see Table 3). The hydrogen bonds are indicated by double-dashed lines. Note the three-coordinate O4 atom and the Zn1-O4-Zn2 bond.



The three Zn atoms form the centers of ZnO_4 tetrahedra (mean $\text{Zn1-O} = 1.943 \text{ \AA}$, mean $\text{Zn2-O} = 1.939 \text{ \AA}$, mean $\text{Zn3-O} = 1.939 \text{ \AA}$). These are somewhat less distorted than the zinc polyhedra in **1** as indicated by the angular variances of 32.2° , 37.4° , and 47.2° , for Zn1, Zn2 and Zn3, respectively. Atoms P1 and P2 (mean $\text{P-O} = 1.534 \text{ \AA}$ and 1.536 \AA , respectively; angular variances = 2.9° and 2.4° , respectively) are the central atoms of essentially regular phosphate groups and all their O atoms link to nearby zinc atoms. Atom P3 (mean $\text{P-O} = 1.534 \text{ \AA}$, angular variance = 14.9°) forms three links to Zn but also possesses a terminal bond to O12. Its length of $1.587(4) \text{ \AA}$ indicates that it must be protonated (*i.e.*, a P-OH species) and the corresponding H atom could indeed be located in a difference map. Geometrical data for **2** are summarized in Table 3.

Table 3. Selected geometrical data (\AA and $^\circ$) for **2**.

Bond	Distance	Bond	Distance
Zn1-O5#1	1.908 (4)	Zn1-O3#2	1.929 (4)
Zn1-O11#2	1.930 (4)	Zn1-O4	2.005 (4)
Zn2-O10	1.909 (4)	Zn2-O7#3	1.929 (4)
Zn2-O2#2	1.952 (4)	Zn2-O4	1.966 (4)
Zn3-O1	1.923 (4)	Zn3-O9#2	1.929 (4)
Zn3-O6	1.944 (4)	Zn3-O8#3	1.959 (4)
P1-O1	1.514 (4)	P1-O2	1.519 (4)
P1-O3	1.530 (4)	P1-O4	1.570 (4)
P2-O5	1.532 (4)	P2-O6	1.537 (4)
P2-O8	1.537 (4)	P2-O7	1.539 (4)
P3-O9	1.509 (4)	P3-O10	1.517 (4)
P3-O11	1.522 (4)	P3-O12	1.588 (4)
Bond	Angle	Bond	Angle
P1-O1-Zn3	139.8 (2)	P1-O2-Zn2#4	131.5 (2)
P1-O3-Zn1#4	131.2 (2)	P1-O4-Zn2	119.0 (2)
P1-O4-Zn1	120.1 (2)	Zn2-O4-Zn1	118.50 (18)
P2-O5-Zn1#5	129.7 (2)	P2-O6-Zn3	132.9 (2)
P2-O7-Zn2#3	130.5 (2)	P2-O8-Zn3#3	132.1 (2)
P3-O9-Zn3#4	136.2 (3)	P3-O10-Zn2	134.4 (3)
P3-O11-Zn1#4	138.6 (3)	—	—

Symmetry codes: (#1) $x, 3/2-y, z-1/2$; (#2) $1-x, y-1/2, 1/2-z$; (#3) $1-x, 1-y, 1-z$; (#4) $1-x, 1/2+y, 1/2-z$; (#5) $x, 3/2-y, 1/2+z$.

In the extended structure of **2**, atom O4 plays an important role in the linking of the tetrahedra, as it forms bonds to Zn1, Zn2 and P1 (bond-angle sum = 357.6°). This results in “dimers” of the zinc species (Figure 4), but the Zn-O-Zn connectivity does not extend any further than this [16]. The mean value of the Zn-O-P bond angle for the other O atoms is 133.7° , almost 10 degrees larger than the corresponding value in **1**.

In the extended structure of **2**, the inorganic layers form infinite (100) sheets containing 4- and 10-rings (Figure 5). The sheets sandwich the H_2dap cations and the extra-layer water molecule (O13) (Figure 6). The water molecule accepts an O-H \cdots O hydrogen bond from the hydrogen phosphate group and also probably forms O-H \cdots O links to framework oxygen atoms. The protonated $-\text{NH}_3^+$

groups of the H₂dap cation form three N-H···O hydrogen bonds each (Table 4), which is a thoroughly typical bonding mode for a protonated amine in a ZnPO [5]. The conformation of the carbon chain of the H₂dap species is somewhat uncertain, but its contorted geometry is clearly different to the extended conformation found for the bridging dap molecules in **1**.

Table 4. Hydrogen bond geometries (Å and °) in **2**.

Bond	D-H	H···A	D···A	D-H···A
O12-H12···O13	0.93	1.77	2.644 (7)	155
N1-H1···O11#6	0.89	2.29	2.915 (9)	127
N1-H2···O12#2	0.89	2.22	2.874 (9)	130
N1-H3···O2#7	0.89	1.92	2.806 (8)	174
N2-H4···O8#2	0.89	1.99	2.823 (6)	155
N2-H5···O3#2	0.89	2.11	2.902 (6)	148
N2-H6···O7#8	0.89	2.01	2.837 (7)	154

Symmetry codes as in Table 3; additionally: (#6) $1+x, y-1, z$; (#7) $2-x, y-1/2, 1/2-z$; (#8) $x, 1/2-y, z-1/2$.

Figure 5. Fragment of a (100) polyhedral sheet in **2** showing 4-ring and 10-ring loops.

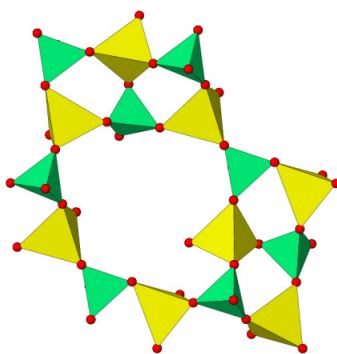
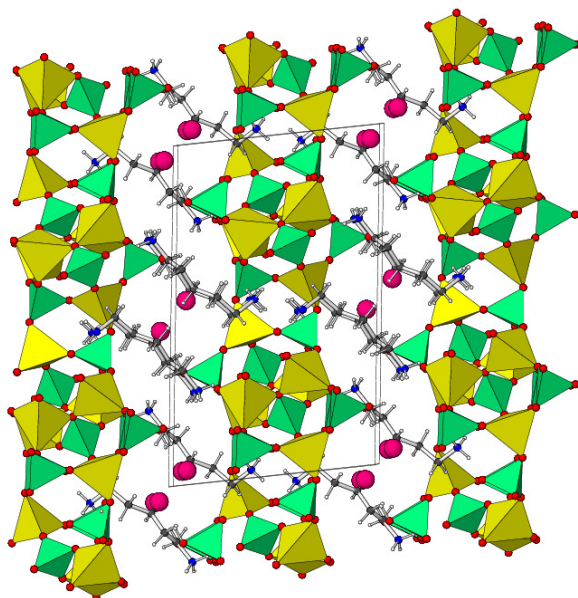


Figure 6. The packing of **2** viewed down [010] showing the (100) inorganic layers sandwiching the organic cations and water molecules (pink spheres); other polyhedron/atom colors as in Figures 2 and 3.



3. Experimental Section

3.1. Synthesis

Compound **1** was prepared from 0.798 g ZnO, 4.9 mL 85% H₃PO₄, 1.00 g dap and 10 mL water (Zn:PO₄:dap ratio = 2:1:2). The components were placed in a 60-mL HDPE bottle and sealed (starting pH \approx 6.0). The bottle was shaken for five minutes and placed in an 80 °C oven for four days. The bottle was removed from the oven and cooled to room temperature over 30 minutes and the solid product, consisting of colorless plates of **1** accompanied by white and brownish powders was recovered by vacuum filtration and rinsing with water and acetone. Compound **2** was prepared from 0.794 g ZnO, 9.8 mL 85% H₃PO₄, 0.51 g dap and 10 mL water (Zn:PO₄:dap ratio = 2:2:1; starting pH \approx 2.0) and subjected to the same heating and product recovery protocol. Pale brown blocks of **2** were recovered, accompanied by some white powder.

3.2. Single-Crystal Data Collection and Analysis

The single-crystal data for **1** (colorless slab, 0.10 \times 0.10 \times 0.02 mm) were collected using a Rigaku Saturn CCD diffractometer at 93 K (Mo K α radiation, λ = 0.71073 Å); the data for **2** (pale brown block, 0.40 \times 0.30 \times 0.24 mm) were collected using a Bruker Kappa APEX II CCD diffractometer (Mo K α radiation, λ = 0.71073 Å) at room temperature. After data reduction, the structures were solved by direct methods with SHELXS and the resulting atomic models were developed and refined against $|F|^2$ with SHELXL [17]. The “observed data” threshold for calculating the $R(F)$ residuals was set as $I > 2\sigma(I)$.

For **1**, the C- and N-bound bound H atoms were placed in idealised locations (C-H = 0.99 Å, N-H = 0.92 Å) and refined as riding atoms. The O-bound (water) H atoms were located in difference maps and refined as riding atoms in their as-found relative locations. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases. The structural model was analysed and validated with PLATON [18] and full refinement details are given in the deposited cif. PLATON indicated considerable pseudo-symmetry corresponding to space group $C2/c$. Trial refinements in this space group, which revealed a number of systematic absence violations, led to essentially the same structure for the framework (albeit with dubious anisotropic displacement parameters) but un-resolvable disorder of the water molecules in the channels. Thus it appears that the symmetry lowering is due to ordering of the water molecules in the channels.

The methylene chain in the H₂dap species in **2** was found to be severely disordered although the terminal -NH₃⁺ groupings were well defined. The application of C-C bond distance restraints led to a geometrically plausible conformation but this cannot be regarded as certain. The H atoms of the water molecule could not be located from difference maps and may be disordered. The C- and N-bound bound H atoms in **2** were placed in idealised locations (C-H = 0.97 Å, N-H = 0.89 Å) and refined as riding atoms. The P-OH H atom was located in a difference map and refined as riding in its as-found relative location. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases. Further refinement details are given in the deposited cif.

Crystal data for **1**: C₁₀H₃₄N₄O₁₁P₂Zn₃, M_r = 644.46, monoclinic, $C2$ (No. 4), Z = 4, a = 25.302 (7) Å, b = 4.9327 (13) Å, c = 19.808 (6) Å, β = 107.377 (8)°, V = 2359.4 (12) Å³, $F(000)$ = 1320,

$T = 93$ (2) K, $\rho_{\text{calc}} = 1.814 \text{ g cm}^{-3}$, $\mu = 3.216 \text{ mm}^{-1}$, 7612 reflections recorded ($3.4^\circ \leq 2\theta \leq 50.7^\circ$; $-30 \leq h \leq 30$, $-5 \leq k \leq 3$, $-23 \leq l \leq 18$), $R_{\text{int}} = 0.047$, 3310 merged reflections, 2728 with $I > 2\sigma(I)$, 273 variable parameters, Flack absolute structure parameter = 0.46 (5), $R(F) = 0.054$, $wR(F^2) = 0.139$, min./max. $\Delta\rho = -1.23, +1.01 \text{ e \AA}^{-3}$. Cambridge Structural Database deposition number: CCDC-883458.

Crystal data for **2**: $\text{C}_5\text{H}_{19}\text{N}_2\text{O}_{13}\text{P}_3\text{Zn}_3$, $M_r = 604.24$, monoclinic, $P2_1/c$ (No. 14), $Z = 4$, $a = 11.3275$ (15) \AA , $b = 8.3235$ (11) \AA , $c = 18.588$ (2) \AA , $\beta = 96.979$ (3) $^\circ$, $V = 1739.6$ (4) \AA^3 , $F(000) = 1208$, $T = 293$ (2) K, $\rho_{\text{calc}} = 2.307 \text{ g cm}^{-3}$, $\mu = 4.447 \text{ mm}^{-1}$, 10734 reflections recorded ($8.7^\circ \leq 2\theta \leq 60.0^\circ$; $-14 \leq h \leq 15$, $-11 \leq k \leq 11$, $-20 \leq l \leq 26$), $R_{\text{int}} = 0.076$, 4954 merged reflections, 3105 with $I > 2\sigma(I)$, 237 variable parameters, $R(F) = 0.056$, $wR(F^2) = 0.119$, min./max. $\Delta\rho = -0.85, +1.97 \text{ e \AA}^{-3}$. Cambridge Structural Database deposition number: CCDC-883459.

4. Conclusions

The crystal structures of $\text{Zn}_3(\text{PO}_4)_2(\text{C}_5\text{H}_{14}\text{N}_2)_2 \cdot 3\text{H}_2\text{O}$ (**1**) and $\text{C}_5\text{H}_{16}\text{N}_2 \cdot \text{Zn}_3(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$ (**2**) have been described. The structure of **1** displays some unusual features for ZnPOs including ZnO_2N_2 and ZnO_3N polyhedra and un-protonated (neutral) template molecules bonding as bridging ligands. This appears to correlate with the relatively high starting pH for the synthesis of **1**, which would presumably favor the presence of un-protonated organic molecules in solution. The structure of $[\text{Zn}_4(\text{HPO}_4)_4(\text{C}_{18}\text{H}_{18}\text{N}_4)_3] \cdot 4\text{H}_2\text{O}$ ($\text{C}_{18}\text{H}_{18}\text{N}_4 = 1,4\text{-bis}(N\text{-benzimidazolyl})\text{butane}$) [11] shares these features, but its overall structure, which features ZnPO chains cross-linked by the ligands, and no obvious channel system, is quite different to that of **1**. The structure of **2**, prepared from a reaction with a lower initial pH, is much more commonplace, and the “multipoint” $\text{N-H}\cdots\text{O}$ hydrogen bonds from the protonated template to the anionic ZnPO sheets have been seen in many other structures [5]. The triply-bridging O atom in the framework of **2** is also a known feature of porous [13] and dense (*i.e.*, non-templated) [19] ZnPOs.

References

1. Vaidhyanathan, R.; Natarajan, S. New open-framework layered tin(II) phosphates intercalated with amines. *J. Mater. Chem.* **1999**, *9*, 1807–1811.
2. Cowley, A.R.; Chippindale, A.M. Synthesis and characterisation of the first unidimensional cobalt hydrogen phosphate $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3][\text{Co}(\text{HPO}_4)_2]$. *J. Chem. Soc. Dalton Trans.* **1999**, *13*, 2147–2149.
3. Jouffret, L.; Rivenet, M.; Abraham, F. A new series of pillared uranyl-vanadates based on uranophane-type sheets in the uranium-vanadium-linear alkyl diamine systems. *J. Solid State Chem.* **2010**, *183*, 84–92.
4. Yang, W.; Li, J.; Xu, J.; Xiong, H.; Wang, L.; Yu, J.; Xu, R. Hydrothermal synthesis of isostructural open-framework manganese and iron borophosphates: Effect of the organic templates in determining the pore shapes. *Solid State Sci.* **2011**, *13*, 757–761.
5. Chidambaram, D.; Neeraj, S.; Natarajan, S.; Rao, C.N.R. Open-framework zinc phosphates synthesized in the presence of structure-directing organic amines. *J. Solid State Chem.* **1999**, *147*, 154–169.

6. Chavez, A.V.; Nenoff, T.M.; Hannooman, L.; Harrison, W.T.A. Tetrahedral-network organo-zincophosphates: Syntheses and structures of $(\text{N}_2\text{C}_6\text{H}_{14})\cdot\text{Zn}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$, $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3\cdot\text{Zn}_2(\text{HPO}_4)_3$ and $(\text{N}_2\text{C}_6\text{H}_{14})\cdot\text{Zn}_3(\text{HPO}_4)_4$. *J. Solid State Chem.* **1999**, *147*, 584–591.
7. Fu, R.; Hu, S.; Wu, X. Mix-solvothermal syntheses, characterization, and properties of new zinc diphosphonates with Zn-O-P chains, layers, and 3D frameworks. *Cryst. Growth Des.* **2007**, *7*, 1134–1144.
8. Rodgers, J.A.; Harrison, W.T.A. $\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3\cdot\text{Zn}_4(\text{PO}_4)_2(\text{HPO}_4)_2\cdot 3\text{H}_2\text{O}$: A novel three-dimensional zinc phosphate framework containing 5- and 20-rings. *J. Mater. Chem.* **2000**, *10*, 2853–2856.
9. Holtby, A.S.; Harrison, W.T.A.; Yilmaz, V.T.; Büyükgüngör, O. New three-dimensional (3,4)-net zincophosphites templated by linear diammonium cations: $\text{H}_3\text{N}(\text{CH}_2)_5\text{NH}_3\cdot\text{Zn}_3(\text{HPO}_3)_4$ and $\beta\text{-H}_3\text{N}(\text{CH}_2)_6\text{NH}_3\cdot\text{Zn}_3(\text{HPO}_3)_4$. *Solid State Sci.* **2007**, *9*, 149–154.
10. Song, H.H.; Zheng, L.M.; Wang, Z.; Yan, C.H.; Xin, X.Q. Zinc diphosphonates templated by organic amines: Syntheses and characterizations of $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]\text{Zn}(\text{hedpH}_2)_2\cdot 2\text{H}_2\text{O}$ and $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{Zn}_2(\text{hedpH})_2\cdot 2\text{H}_2\text{O}$ ($n = 4, 5, 6$) (hedp = 1-hydroxyethylidenediphosphonate). *Inorg. Chem.* **2001**, *40*, 5024–5029.
11. Fan, J.; Hanson, B.E. Novel zinc phosphate topologies defined by organic ligands. *Inorg. Chem.* **2005**, *44*, 6998–7008.
12. Robinson, K.; Gibbs, G.V.; Ribbe, P.H. Quadratic elongation-quantitative measure of distortion in coordination polyhedra. *Science* **1971**, *172*, 567–570.
13. Harrison, W.T.A.; Nenoff, T.M.; Eddy, M.M.; Martin, T.E.; Stucky, G.D. Organic templates in zincophosphate synthesis— $\text{Zn}_5(\text{PO}_4)_2(\text{HPO}_4)_4\cdot\text{H}_2\text{O}\cdot 2\text{H}_2\text{N}_2\text{C}_6\text{H}_{12}$ containing two distinct 8-ring channels and $\text{Zn}_3(\text{PO}_4)(\text{HPO}_4)_2\cdot\text{HN}_2\text{C}_6\text{H}_{12}$ containing tetrahedral 3-rings and Zn-N bonds. *J. Mater. Chem.* **1992**, *2*, 1127–1134.
14. Belhouchet, M.; Savariault, J.M.; Mhiri, T. Crystal structure and thermal behavior of two new organic monosulfates $\text{NH}_3(\text{CH}_2)_5\text{NH}_3\text{SO}_4\cdot 1.5\text{H}_2\text{O}$ and $\text{NH}_3(\text{CH}_2)_9\text{NH}_3\text{SO}_4\cdot\text{H}_2\text{O}$. *J. Phys. Chem. Solids* **2005**, *66*, 1294–1301.
15. Mandal, S.; Natarajan, S. Solvothermal synthesis and structures of one- and two-dimensional zinc phosphates. *Inorg. Chim. Acta* **2004**, *357*, 1437–1443.
16. Harrison, W.T.A.; Rodgers, J.A.; Phillips, M.L.F.; Nenoff, T.E. In situ template generation for zincophosphate synthesis leading to guanylurea zinc phosphate, $\text{C}_2\text{H}_7\text{N}_4\text{O}\cdot\text{ZnPO}_4$, containing template-to-template N–H–O hydrogen bonds. *Solid State Sci.* **2002**, *4*, 969–972.
17. Sheldrick, G.M. A short history of SHELX. *Acta Cryst.* **2008**, *A64*, 112–122.
18. Spek, A.L. Structure validation in chemical crystallography. *Acta Cryst.* **2009**, *D65*, 148–155.
19. Nenoff, T.M.; Harrison, W.T.A.; Gier, T.E.; Calabrese, J.C.; Stucky, G.D. The low-temperature synthesis and characterization of two layered materials containing 3-ring groupings: $\text{NaH}(\text{ZnPO}_4)_2$ and $\text{CsH}(\text{ZnPO}_4)_2$. *J. Solid State Chem.* **1993**, *107*, 285–295.